

METHOD FOR MAKING A BLOCKED AMINE**CROSS-REFERENCE TO RELATED APPLICATION**

5 This application is a divisional of U.S. patent application serial number 09/776,489 filed February 2, 2001, entitled "SINGLE COMPONENT ROOM TEMPERATURE CURABLE LOW VOC EPOXY COATINGS".

BACKGROUND OF THE INVENTION

10 The present invention relates generally to epoxy coatings, and more particularly to the use of blocked amine compounds in making epoxy coatings.

Curable epoxy resin systems are known. Conventional two component epoxy resin systems involve mixing of the epoxy resin and hardener and subsequent application of such mixtures as coatings by various techniques. Once mixed, such systems have short pot lives and 15 must be used within a few hours.

As a result, efforts have been made to develop what are called one component systems. In one component systems, the curing agent is mixed with the epoxy but is inactive. It can be activated at a later time. One type of one component system involves the use of elevated temperature to activate the cross-linking reaction. However, the use of high temperatures is 20 undesirable in many applications.

Another type uses latent cure, blocked amine systems in an attempt to alleviate the problem of reduced shelf life. In blocked amine systems, the amine is reacted with a ketone or aldehyde to form a blocked amine which is mixed with the epoxy resin. The system is activated by the addition of water, typically in the form of ambient moisture. This reverses the blocking 25 reaction, forming the amine and the ketone or aldehyde. The amine then reacts with the uncured epoxy resin, and the ketone or aldehyde either evaporates or co-reacts with the epoxy. In the absence of moisture, such blocked amines systems afford a slight improvement in storage stability over conventional two component systems. However, commercial ketimine-based

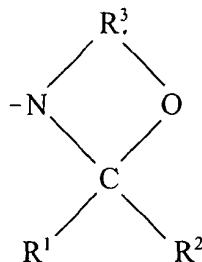
epoxy resin systems still suffer from limited storage stability, typically having a pot life of less than 24 hours. (Shell, 1986, EPON Curing Agents).

Furthermore, many systems include volatile organic compounds (VOC) or hazardous air pollutants (HAP), which are regulated. Commercial ketimine-based epoxy resin systems have elevated levels of VOCs, generally in excess of 3.5 lbs/gal. Under the current VOC standard for many industrial and maintenance coating applications, the limit is 3.1 lbs/gal of VOCs. This limit is likely to be reduced in the future to less than 2.8 lbs/gal of VOCs.

The use of ketimines as curing agents for epoxy resins is described in R.T. Holm, "Ketimines as Latent Epoxy Curing Agents," J. of Paint Tech., Vol. 39, No. 509, June 1967, pp. 385-388. The VOC levels of these compounds is over 3.5 lbs/gal. The reported viscosity of the formulations containing the various ketimines ranged from about 3 to about 36 stokes after storage for 20 days at 25°C. However, these formulations do not provide the long term stability desired for commercial products. The long term stability of the formulations can be evaluated using accelerated aging testing at 55°C. Two weeks storage at 55°C is equivalent to a shelf life of about six months, while 30 days storage is equivalent to a shelf life of over 1 year. The shelf life at 55°C is estimated to be only about 12% of the value at 25°C.

British Patent No. 960,236, which is incorporated herein by reference, attempts to improve the shelf life of ketimine-based single component epoxy coatings by using hydroxyl-containing imines as blocked curing agents. The imines are obtained by reacting one or more imines possessing at least one amino hydrogen and one or more compounds having at least one epoxy group. No shelf life or VOC level is reported for these formulations. U.S. Patent No. 5,837,785, which is incorporated herein by reference, discloses the use of heterocyclic containing curing agents for use in single component epoxy resin compositions. The heterocycle-containing compound has a backbone chain selected from the group consisting of polyether, polyvinyl, polyester, polyamide, polycarbonate, and novolac chains and at least two heterocyclic groups of the following general formula as side chains:

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wherein R¹ and R² may be the same or different and each represents hydrogen, straight chain or branched C₁ to C₆ alkyl or alkenyl, or C₆ to C₈ aryl; or R¹ and R² taken together with the adjacent carbon atom, represents C₅ to C₇ cycloalkyl; R³ represents C₁ to C₁₀ alkylene. A shelf life of 6 months at 40°C is reported, but no VOC level is given. The viscosity of coating formulations is not disclosed, but it appears to be high for conventional coating applications.

Therefore, there is a need for a single component epoxy coating precursor having improved shelf life and a method for making such a precursor. There is also a need for a low VOC epoxy coating and for a method of making such a coating. There is also a need for a method of making a blocked amine which can be used in a single component epoxy coating precursor.

SUMMARY OF THE INVENTION

The present invention solves this need by providing a single component epoxy coating precursor and a method for making such a precursor, a low VOC epoxy coating and a method for making such a coating, and a method for making a blocked amine which is more stable than previously known ones.

The single component epoxy coating precursor includes an epoxy resin, a first solvent, and a blocked amine. The single component epoxy coating precursor has a viscosity after 30 days at a temperature of 55°C of less than 16 stokes. It can have a viscosity after 30 days at a temperature of 55°C of less than 13 stokes, or a viscosity after 30 days at a temperature of 55°C of less than 7 stokes.

The method for making a single component epoxy coating precursor includes drying an epoxy resin and a blocked amine, combining and mixing the epoxy resin, the blocked amine, and a first solvent to form the single component epoxy coating precursor, wherein the single component epoxy coating precursor has a viscosity after 30 days at a temperature of 55°C of less than 16 stokes. It can have a viscosity after 30 days at a temperature of 55°C of less than 13 stokes, or a viscosity after 30 days at a temperature of 55°C of less than 7 stokes. This level of viscosity stability at 55°C generally corresponds to over one year of shelf life at room temperature storage conditions.

A reactive diluent optionally can be added to the single component epoxy coating precursor. Reactive diluents include, but are not limited to, modified glycidyl ethers, acrylates, methacrylates, urethane acrylates and combinations thereof. A water scavenger optionally can be added to the single component epoxy coating precursor. Water scavengers include, but are not limited to, molecular sieves, monocyclic bifunctional oxazolidines and combinations thereof. Pigments may be optionally added to the single component epoxy coating precursor. Pigments include, but are not limited to, titanium dioxide, diarylide yellow, iron oxide, raw umber, burnt umber, phthalocyanine blue, cobalt blue, chinese blue, phthalocyanine green, toluidine red, quinacridone red, dicerylide orange, carbon black, furnace black, lampblack, leafing aluminum and non-leaving aluminum.

Other formulating aids such as wetting agents, flow and rheology modifiers, light stability additives, etc., known in the art can be also incorporated.

First solvents which are useful in the present invention include, but are not limited to acetone, p-chlorobenzotrifluoride, t-butyl acetate, methyl isobutyl ketone, methyl propyl ketone and combinations thereof.

Epoxy resins include, but are not limited to, aliphatic epoxy resins, cycloaliphatic epoxy resins, aromatic epoxy resins and combinations thereof.

The single component epoxy coating precursor can have a VOC level of less than about 3 lbs/gal, or a VOC level of less than about 2.8 lbs/gal.

The method of making a low VOC epoxy coating includes drying an epoxy resin and a blocked amine, combining and mixing the epoxy resin, the blocked amine, and a first solvent to form the single component epoxy coating precursor, the single component epoxy coating precursor having a VOC level of less than about 3 lbs/gal, and exposing the single component 5 epoxy coating precursor to water, the single component epoxy coating precursor and water reacting to form the low VOC epoxy coating. The water can be present in any form desired, including, but not limited to liquid water, and moisture in the air. The VOC level can be less than about 2.8 lbs/gal. The single component epoxy coating precursor described above and the blocked amine described below can be used to make the low VOC epoxy coating.

10 The method for making the blocked amine includes mixing a solvent capable of forming an azeotrope with water, an amine, and an amine blocker selected from ketones and aldehydes in a reaction vessel to form a reaction mixture. Ambient moisture is removed from the reaction vessel. The amine and the amine blocker are reacted to form the blocked amine and water of reaction, and the water of reaction is removed from the reaction mixture while the amine and the 15 amine blocker are reacted. The blocked amine is recovered while maintaining the absence of moisture.

The solvent capable of forming an azeotrope with water includes solvents which can form binary or ternary azeotropes with water. These include, but are not limited to, toluene, xylene and combinations thereof.

20 The amine can be a polyamine, and it includes but is not limited to, diethylenetriamine, m-xylylenediamine and combinations thereof.

The amine blocker is selected from ketones and aldehydes. The ketones and aldehydes may have a molecular weight in the range of about 30 to about 600. They may have between about 2 and 14 carbon atoms. Suitable ketones include, but are not limited to, methyl isobutyl 25 ketone, methyl ethyl ketone, acetone, phorone, heptanedione, tetramethylheptanedione, adamantone, acetonyl acetone, methylpropylketone and combinations thereof. Suitable aldehydes include, but are not limited to benzaldehyde, salicylaldehyde and combinations thereof.

The yield of blocked amine can be greater than about 90% of the theoretical yield, or greater than about 95% of the theoretical yield, or greater than about 97% of the theoretical yield.

The low VOC epoxy coating includes a reaction product of a single component epoxy coating precursor and water, the single component epoxy coating precursor comprising an epoxy resin and a blocked amine, the single component epoxy coating precursor having a VOC level of less than about 3 lbs/gal. The low VOC epoxy coating can have a VOC level of less than about 2.8 lbs/gal.

DETAILED DESCRIPTION OF THE INVENTION

The blocked amines were prepared according to the following procedure. The chemicals to be used were dried over molecular sieves. A solvent capable of forming an azeotrope with water was placed in a suitably sized round bottom flask fitted with a stir bar, magnetic stir plate, heating mantel, reflux condenser, and a Dean-Stark tube. The solvent capable of forming an azeotrope with water includes, but is not limited to, solvents which can form binary or ternary azeotropes with water. Examples of suitable solvents include, but are not limited to, toluene, xylene and combinations thereof. Toluene was used in these experiments as the solvent capable of forming an azeotrope with water. However, it is to be understood that other solvents capable of forming azeotropes with water could also be used. The flask was charged with an amine, a ketone or aldehyde, and a catalyst. Any appropriate catalyst can be used. Generally, acid based catalysts are used, such as p-toluene sulfonic acid. The neck of the reaction flask was wiped with a small amount of toluene to remove any trace reactants. The flask walls were also rinsed with a small amount of toluene to minimize exposure of the reactants to ambient moisture.

After the reaction mixture was added to the flask, it was purged under a stream of argon for about 5 minutes while stirring to remove ambient moisture and oxygen. The reflux condenser was quickly put in place and fitted with a gas inlet tube to provide a very slight positive pressure. Alternatively, the reflux condenser can be fitted with a drying tube containing DrieriteTM to avoid incorporation of atmospheric water during the reaction or the subsequent cooling period before the flask is transferred to a distillation apparatus, such as a RotovapTM. No significant difference

was observed in the efficiency of azeotrope or the theoretical mass of water recovered using either arrangement.

Water flow to the condenser was started, and the reaction flask and the Dean-Stark tube were wrapped in foil to improve water azeotroping efficiency. The reaction mixture was then 5 stirred and heated. The mixture was maintained under steady state conditions at about 116°C while stirring until either 100% of the theoretical water of reaction was recovered or until water ceased to azeotrope. The temperature will depend on the particular solvent used, and it should be about the boiling point of the solvent. Here, with toluene as the solvent (BP about 111°C), the temperature was about 116°C. Water was drained from the Dean-Stark tube as required to 10 prevent overfilling. The water of reaction recovered was over 90% of the theoretical amount, typically over 95%, and generally in the range of 96% to 99%.

At the end of each run, the reaction flask was cooled overnight to room temperature under a slight increase in initial argon pressure or with the drying tube in place. The positive increase in argon pressure was to prevent the transport of trap oil and moisture into the reaction flask.

15 After cooling to room temperature, the reaction mixture was placed in a Rotovap™ to remove toluene and any unreacted ketone or aldehyde. The bath temperature was 70°C, and the vacuum was increased slowly to about 2 mm Hg over one hour. The reaction flask was returned to ambient pressure under argon, removed from the Rotovap™, and placed in a vacuum oven for two days at 70°C and about 2 mm Hg to remove any remaining traces of toluene, ketone, or 20 aldehyde. Heat to the vacuum oven was turned off, and the flask was cooled to ambient temperature while maintaining a vacuum. Under a stream of argon, the flask was returned to ambient pressure, placed over mole sieves, and capped. The reaction product was evaluated by infrared analysis for free amine.

Amines made using this procedure were blocked with a variety of different ketones and 25 aldehydes. These blocked amines were then used to make single component epoxy resin precursors. The properties of the precursors and the coatings made from them were then evaluated.

The viscosity of the single component epoxy coating precursors in two solvents, toluene and methylisobutylketone (MIBK), at ambient temperature was monitored. In addition, the viscosity was monitored for the epoxy coating precursors in MIBK at 55°C. The accelerated aging samples were tested on a daily basis for the first 30 days, except on weekends, in order to 5 determine viscosity. The process included removing the samples from the oven, cooling the samples to room temperature, and then measuring the samples in direct comparison with Gardner bubble viscosity tubes. The Gardner bubble viscosity tubes use bubble velocity to determine the viscosity of a sample. The viscosity of the sample is determined by finding the standard tube of known viscosity where the air bubble rises at the same rate with that of the test sample. A 10 viscosity of less than 16 stokes is desirable because formulations remain sprayable with conventional spray equipment at this viscosity.

Coating properties were also evaluated. Draw-down panels were prepared using a #54 wire bound rod over Bonderite iron phosphate treated 3" x 6" x 0.0032" steel panels and stored at 23°C and 50% relative humidity to evaluate cure time and the physical properties of the films.

15 The pencil hardness test is described in Paint Testing Manual by H.A. Gardner and G.G. Sward, 13th Ed. (1972) p. 283-284, which is incorporated herein by reference. The ratings from worst to best are: 6B, 5B, 4B, 3B, 2B, B, HB, F, H, 2H, 3H, 4H, 5H, and 6H.

20 For the MEK double rubs, a pad made from 10 plies of gauze material is attached to the ball end of a 2 lb ball peen hammer. The pad is saturated with methyl ethyl ketone (MEK) and rubbed across the coated substrate. A constant back and forth motion is used so that only the weight of the hammer applies the force. One double rub is equal to one back and forth movement. The movement is continued until the film is marred and/or begins to be removed by the solvent. One hundred double rubs are required to pass this test.

Other standard tests were also run.

25 Table 1 shows the formulation of the blocked amine and the epoxy coating precursor, and Tables 2 and 3 show the results of the initial evaluation of the epoxy coating precursors and the epoxy coatings.

The control formulation containing unblocked diethylenetriamine (DETA) cured in 2 hrs as a thin film from MIBK. The bottled control in toluene gelled in 24 hrs, while the control in MIBK gelled in 48 hours under ambient conditions. The control in MIBK stored at 55°C gelled between 1 and 18 hrs.

5 In Run 1, an experimental DETA-based curing agent blocked with acetone was used. The experimental DETA-based curing agent was supplied by Shell with the designation S42686, and contained a mixture of DETA, a proprietary amine, and an alkyl phenol amine (hereafter referred to as "experimental DETA"). The film dried to the touch between 0-24 hrs. The toluene and MIBK formulations stored at room temperature gelled in 7 days and 9 days, respectively. The 10 accelerated aging sample gelled within 24 hrs.

In Run 2, the experimental DETA-based curing agent was blocked with MIBK. The drying time for this film was 0-24 hrs. Additional films were prepared from this formulation after 3 weeks of aging at room temperature and after 16 days at 55°C. The films were dry to the touch at 6 hrs and 2 hrs. The films made from the aged formulations were blush-free and showed 15 increased gloss with aging of the bottled formulations. Both samples stored at room temperature remained water like with no change in viscosity. The accelerated aging sample showed no change in viscosity until after 15 days. At that time, the viscosity went from about 0.5 to 4.4 stokes within 24 hrs. The sample remained pourable for 2 more days. Gel time was between 17 and 19 days. A replicate sample gelled in 22-24 days with a similar cure profile.

20 Run 4 used reagent grade DETA blocked with acetone. The drying time was slow, over 48 hrs, and the accelerated aging sample gelled in less than 24 hrs. These results are similar to the ones with experimental DETA. (Run 2).

25 DETA (reagent grade) blocked with MIBK was used in Run 5. Two panels were prepared from this formulation, one fresh and the other aged for two days. The drying time for the first panel was 0-24 hrs. The first panel showed a slight blush and a low gloss on cure. The second panel was monitored at 2 hr intervals to more accurately assess drying time. It was dry to the touch in 4 hrs, and showed no blush and excellent gloss (the wet look) after cure. The bottled

samples stored at room temperature remained water like for over 8 weeks. The accelerated aging sample gelled after 24 days. A replicate sample also gelled in about 24 days.

In Run 6, lysine $[H_2N(CH_2)_4CH(NH_2)COOH]$ was blocked with MIBK. One panel containing a 5% excess of blocked amine based upon 4 primary amines, and another containing a 5% excess based on all reactive hydrogens (typically 5) were prepared. The panels remained tacky after 8 hrs, but were dry to the touch the next morning. Pencil hardness was B at 24 hrs and 1 week. The panels showed poor resistance to MEK. The accelerated aging samples showed no increase in viscosity after 29 days. The sample with the lower concentration of blocked amine gelled in less than 6 months, while the sample with the higher level gelled in less than 5 months.

Run 7 involved the use of DETA blocked with phorone $[(CH_3)C=CHCOCH=C(CH_3)_2]$. Films were dry to the touch in about 8 hrs. The panel containing less blocked amine required 8-10 hrs. Pencil hardness was <B after 24 hrs and 1 week, and solvent resistance was poor. The accelerated aging sample containing the lower level of blocked amine gelled in 25 days. The sample with the higher concentration of blocked amine gelled in 14 days.

In Run 8, DETA blocked with 2-heptanedione $[CH_3(CH_2)_4COCH_3]$ was used. The films were dry to the touch in 8 hrs. Pencil hardness was B at 24 hrs increasing to F at 1 week. MEK resistance was good, especially for the sample with the higher concentration of blocked amine. The panels were glossy with a slight blush. The mixtures exhibited "crawling" during application. "Crawling" refers to coatings that draw away from the surface and leave holes or voids in the coating. Such bare areas are usually related to the wetting properties of the formulation. The accelerated aging sample with the lower concentration of blocked amine gelled in 25 days, while the sample with the higher concentration gelled at 14 days.

DETA blocked with tetramethyl heptanedione $[(CH_3)_3CCOCH_2COC(CH_3)_3]$ was used in Run 9 to evaluate the performance of a diketone. The panels required more than 48 hrs to cure and exhibited inadequate hardness and solvent resistance. The accelerated aging samples showed no change in viscosity after 29 days, and did not gel for more than 6 months.

In Run 10, panels made with DETA blocked with pyruvic aldehyde dimethyl acetyl were tacky, but nearly dry to the touch after 8 hrs, and they were completely dry the next morning.

Pencil hardness was B after 24 hours for the lower concentration of the blocked amine, and it was F after 1 week. The panel made from the higher concentration had a pencil hardness that was <B and H for the same time intervals. The solvent resistance was 100 double rubs after 1 week. The panels had a good gloss and light blush. The sample with the higher concentration of 5 blocked amine showed a change in viscosity from 0.5 to 13 strokes after 14 days of accelerated aging, and gelled in 17 days. The sample with the lower concentration gelled after more than 30 days.

Run 11 involved the use of DETA blocked with adamantone. After 8 hours, the panels were dry to the touch. The pencil hardness was H, and the MEK resistance was 100 double rubs 10 after one week. The films were medium amber with a gloss <90 and a slight blush. The viscosity of the formulation with the lower concentration of blocked amine, increased from 0.5 to 4 strokes in 14 days, and it gelled at between 16 and 21 days. The formulation having the higher concentration of blocked amine gelled in 13 days.

In Run 12, DETA blocked with acetonyl acetone [$\text{CH}_3\text{COCH}_2\text{CH}_2\text{COCH}_3$] was used. 15 The panels remained soft and too tacky for physical evaluation after one week. After 28 days, no change in viscosity was found in the accelerated aging samples.

Meta-xylylenediamine blocked with MIBK was used in Run 13. Within 8 to 9 hours the panels were dry to the touch. According to the literature, blocked amines prepared from meta-xylylenediamine and MIBK dry to the touch in 4 hours at room temperature in the presence of a 20 phenol accelerator. The pencil hardness for the lower concentration of blocked amine was B after 24 hrs, HB after 48 hrs, and HB after 72 hrs. The MEK double rubs were 50 after 24 hrs, 100 after 48 hrs, and 100 after 72 hrs. The panel passed the direct impact tasting, cross hatch and 1/4 inch mandrel bend test. The panel showed good gloss and appearance. The panel containing 25 the higher concentration of blocked amine showed a pencil hardness of F after 24 hrs, F after 48 hrs, and H after 72 hrs. The MEK double rubs results were 90 after 24 hrs, 100 after 48 hrs, and 100 after 72 hrs. This panel also passed the direct impact, cross hatch and 1/4 inch mandrel bend tests. No viscosity change occurred until after 30 days of accelerated aging. The formulation with the lower concentration of blocked amine remained unchanged after 40 days of accelerated

aging and did not gel for more than 6 months. The formulation having the higher concentration of blocked amine had a viscosity of 2.8 stokes after 40 days, and it did not gel for more than 4.5 months.

5 Run 14 involved xylylenediamine blocked with diisobutylketone (DIBK). Both panels required more than 48 hrs to dry. They showed a pencil hardness of B after one week. At one week, the MEK double rubs were 20 for the lower concentration and 100 for the higher concentration. The panel passed the other tests. The films were water white with a gloss >90. The aging samples remained unchanged after 13 days.

10 In summary, Runs 2, 5, 7, 8, 11, and 13 resulted in thin film cure times of 8 hrs or less. Runs 7, 8, and 11 had reasonable viscosity stability at 55°C. The films that produced the best 15 overall physical properties, cure rate, and with over 20 days of viscosity stability at 55°C were Runs 2, 5, and 13.

15 From these studies, we found that the effectiveness of the blocking agent in providing long term stability for the single component epoxy coating precursors varies depending on the molecular weight of the blocking agents. A blocking agent having a molecular weight in the range of 30 to 600 provides good long term stability.

20 The blocked amine used in Run 5, DETA blocked with MIBK, was also evaluated with the addition of titanium dioxide (TiO₂). Three formulations of DETA blocked with MIBK were tested under accelerated aging conditions: 3.5 g of DETA blocked with MIBK without TiO₂, 3.5 g of DETA blocked with MIBK with 13% TiO₂, and 3.8 g of DETA blocked with MIBK with 13% TiO₂. The formulations containing TiO₂ gelled in 18 days, as compared to 24 days for the sample without TiO₂. The 3.5 g of DETA blocked with MIBK with 13% TiO₂, was slower to cure than the control. However, by increasing the concentration of the blocked amine (3.8 g of DETA), a slight improvement in thin film cure times and physical properties occurred. Results 25 are further described in Table 4.

Tests were run with reduced solvent (VOC) levels. The results are shown in Table 5 with regard to storage stability, thin film set time and the physical properties of formulations. Similar results occurred for cure and physical properties regardless of the solvent level. The data showed

that under accelerated aging conditions, a sample containing half the MIBK concentration gelled in 12 to 14 days, compared to about 24 days for the normal level of MIBK in the control. The control contained 4.0 lbs/gal volatiles while the reduced solvent formulations contained 2.8 lbs/gal of volatiles.

Table 1: Formulations

Run	Control	1	2A	2B	2C	4
Amine	DETA	DETA-based experimental amine	DETA-based experimental amine	DETA-based experimental amine	DETA-based experimental amine	DETA
Blocking Agent		Acetone	MIBK	MIBK	MIBK	Acetone
Draw-down Formulation						
Solvent	MIBK	MIBK	MIBK	MIBK	MIBK	MIBK
Epoxy resin						
Blocked Amine						
Aging			None	3 weeks at RT	16 days at 55 °C	

Run	5A	5B	6A	6B	7A	7B
Amine	DETA	DETA	Lysine	Lysine	DETA	DETA
Blocking Agent	MIBK	MIBK	MIBK	MIBK	Phorone	Phorone
Draw-down Formulation						
Solvent			MIBK - 10 g			
Epoxy resin			10 g	10 g	10 g	10 g
Blocked Amine			3.55 g	4.42 g	3.98 g	4.96 g
Aging						

Table 1 (cont'd)

Run	8A	8B	9A	9B	10A	10B
Amine	DETA	DETA	DETA	DETA	DETA	DETA
Blocking Agent	2-heptanone	2-heptanone	tetramethyl heptanedione	tetramethyl heptanedione	pyruvic aldehyde dimethyl acetal	pyruvic aldehyde dimethyl acetal
Draw-down Formulation						
Solvent	MIBK - 10 g	MIBK - 10 g	MIBK - 10 g	MIBK - 10 g	MIBK - 10 g	MIBK - 10 g
Epoxy resin	10 g	10 g	10 g	10 g	10 g	10 g
Blocked Amine	3.42 g	4.26 g	5.05 g	6.28	3.51 g	4.38 g
Aging						

Run	11A	11B	12 A	12B	13 A	13B
Amine	DETA	DETA	DETA	DETA	Xylylenediamine	Xylylenediamine
Blocking Agent	Adamantone	Adamantone	Acetonyl acetone	Acetonyl acetone	MIBK	MIBK
Draw-down Formulation						
Solvent	MIBK - 10 g	MIBK - 10 g	MIBK - 10 g	MIBK - 10 g	MIBK - 10 g	MIBK - 10 g
Epoxy resin	10 g	10 g	10 g	10 g	10 g	10 g
Blocked Amine	4.26 g	5.30 g	3.42 g	4.26 g	3.5 g	4.3 g
Aging						

Table 1 (cont'd)

Run	14A	14B
Amine	Xylylenediamine	Xylylenediamine
Blocking Agent	DIBK	DIBK
Draw-down Formulation		
Solvent	MIBK - 10 g	MIBK - 10 g
Epoxy resin	10 g	10 g
Blocked Amine	4.41 g	5.49 g
Aging		

Table 2: Evaluation Blocked Amines

Run	Time (hrs)	Dry to Touch	Pencil Hardness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
Control	2 hrs												
24	2H	Passed (100)											
48	3H												
168-wk				Passed (100)	Passed	Passed	Some linear failure; no squares		Very slight stress cracking				

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hard- ness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/ 24 hrs)	MBK at RT (Daily/ 24 hrs)	MBK at 55°C (Daily/ 24 hrs)
1	0-24 hrs												
	24	2H	51, softening; 24 hr full recovery										Gelled in 24 hrs
	48			Passed (100)									
	168- wk	2H		Passed (100)	Passed	Partial "rim" failure	Passed	Failed; lost adhesion			Gelled in 7 days	Gelled in 9 days	

Table 2 (cont'd)

Table 2 (cont'd)

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hard- ness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/ 24hrs)	MIBK at RT (Daily/ 24hrs)	MIBK at 55°C (Daily/ 24 hrs)
2C	2 hrs												
2	Dry to touch, slight FP									Light amber no blush high gloss (wet look)			
4	Dry to touch, slight FP												
6	Dry to touch, slight FP												
8	Dry to touch, slight FP, recovers												
24													
48/72				HB	80	Pass d	Pass d		Passed				
96				HB	90								
1 wk				F	100	Pass d	Pass d		Passed				

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hard- ness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1 wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
4	24-48 hrs?								Mod amber mod blush orange peel				Water like
24	Tacky	HB	42										Gelled in 24 hrs
48/72	Weekend	HB	60/75										
96	Dry		75										
	1 wk		F	100	Passed	Passed	Slight failure			No change			
	2 wk										Not moni- tored		

Table 2 (cont'd)

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hard- ness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1 wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
5B	4 hrs												
	2	Wet											
	4	Dry to touch, slight FP											
	6	Dry to touch, slight FP											
	8	Dry to touch, no FP											
	24									Clear high gloss no brush			
	1 wk				Passed	Slight "rim" failure	Passed						Gelled in about 24 days

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hardness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/24 hrs)	MIBK at RT (Daily/24 hrs)	MIBK at 55°C (Daily/24 hrs)
6A		8-24 hrs											
	24	Dry to touch, slight FP	<B	<10									
		1 wk	B	15	Passed	Passed	Passed	Passed	Water white dull slightly bluish				Gelled in less than 5 months
Run	Time (hrs)	Dry to Touch	Pencil Hardness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/24 hrs)	MIBK at RT (Daily/24 hrs)	MIBK at 55°C (Daily/24 hrs)
6B		8-24 hrs											
	24/48		B	20									
		72/96											Gelled in less than 6 months
		1 wk	B	15	Passed	Passed	Passed	Passed	Water white dull slightly bluish				

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hardness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1 wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
7A	8-10 hrs												
	24	<B	<5										
	1 wk	<B	6	Failed	Failed	Passed	Passed	Passed	Dark amber	>90			Gelled in 25 days
7B	8 hrs												
	24		<B	<5									
	1 wk	B	6	Failed	Failed	Passed	Passed	Passed	Dark amber	>90			Gelled in 14 days

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hard- ness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1 wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
8A	7 hrs											
8	7 hrs dry to touch very slight FP											
24		B	10									
1 wk		F	100 (dulled film)		Passed	Failed	Passed	Passed	Yellow medium amber blush	<90		Gelled in 14 days

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hard- ness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1 wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
8B	6 hrs												
	6	dry to touch very slight FP											
	24		B	100 (dulled film)									
	1 wk		F	100 (no effect)	Passed	Failed	Passed	Failed	Yellow medium amber blush	<90			Gelled in 25 days

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hard- ness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1 wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
9A		>48 hrs											
	24	Tacky, FP	Gummy	Gummy									
	1 wk		<B	10	Passed	Passed	Passed	Passed	Water white	>90			
													Gelled in more than 6 months
Run	Time (hrs)	Dry to Touch	Pencil Hard- ness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1 wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
9B		>48 hrs											
	24	Tacky, FP	Gummy	Gummy									
	1 wk		<B	15	Passed	Passed	Passed	Passed					
													Gelled in more than 6 months

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hardness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
10A	8-24 hrs												
	8	nearly dry											
		B	<10										
	1 wk	F	100 (dulled film)		Passed	Passed		Passed	Light amber blush	>90			Gelled in more than 30 days
Run	Time (hrs)	Dry to Touch	Pencil Hardness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
10B	8-24												
	8	nearly dry											
	24		<B	5									
	1 wk	H	100 (dulled film)		Passed	Passed		Failed	Light amber	<90			Gelled in 17 days

Table 2 (cont'd)

Table 2 (cont'd)

Table 2 (cont'd)

Run	Time (hrs)	Dry to Touch	Pencil Hardness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
14A	> 48 hrs												
	24	Sticky	Sticky										
	1 wk	B	20	Passed	Passed	Passed	Passed	Passed	Water white	>90			
Run	Time (hrs)	Dry to Touch	Pencil Hardness	MEK Dbl. Rubs	20 lbs	40 lbs	Cross Hatch Adhesion	1/4" Mandrel Bend	Film Color (1 wk)	Gloss (1wk)	Toluene at RT (Daily/ 24 hrs)	MIBK at RT (Daily/ 24 hrs)	MIBK at 55°C (Daily/ 24 hrs)
14B	> 48 hrs												
	24	Sticky	Sticky										
	1 wk	B	100 (slight dulling)	Passed	Passed	Passed	Passed	Passed	Water white	>90			

Table 3: Overall Film Evaluations Based on Visual Observation

Run	Comments
4	Moderate blush
6A	Excellent flow upon application, gloss diminished after 8 hrs
6B	Excellent flow upon application, gloss diminished after 8 hrs
7A	Good flow upon application, slight fisheyes
7B	Good flow upon application, slight fisheyes
8A	Poor flow, crawling
8B	Poor flow, crawling
9A	Fairly good flow, slight crawling
10A	Good flow upon application
10B	Good flow upon application
11A	Good flow upon application
11B	Good flow upon application
12A	Poor flow upon application, crawling, fisheyes
12B	Poor flow upon application, crawling, fisheyes
14A	Very good flow upon application
14B	Very good flow upon application
15A	Good flow upon application
15B	Good flow upon application

Table 4: Physical Data for Epoxy Formulations With and Without Titanium Dioxide

Table 4: (cont'd)

Hardness (24 hours)		FORMULATION			Dry to touch			MEK Double Rubs			Gel time
Ingredients	Grams	(hours)	Day 1	Day 5	Day 6	Day 1	Day 5	Day 6	(days)	Comments	
48262-41-28		4 hours,	2H								
>4.0 VOC		DTT, FP									
MIBK-DETA	3.8									Passed direct impact, cross hatch and 1/4" mandrel bend testing, gloss and appearance excellent	
MIBK	10										
EPON 828	10										
TiO ₂		~ 13%									

^a No gel time taken for this sample used gel time for identical formulation 48220-44-09^b No gel time taken for this sample used gel time for identical formulation prepared with dried TiO₂ 48220-65-07

Table 5: Physical Data for Epoxy Formulations With Different Concentrations of MIBK

FORMULATION		Dry to touch	Hardness (24 hours)		MEK Double Rubs	Gel time	Comments
Ingredients	Grams		Day 1	Day 5	Day 6	Day 6	(days)
Run 2							
48262-38-07 3.9 VOC							
MIBKxp-DETA	3.5	6 hours	B	H	40	100	
MIBK	10	DTT. Very slight FP					
EPON 828	10						
48262-38-25 2.98 VOC							
MIBKxp-DETA	3.5	9 hours	<B	F	80	100	
MIBK	5	DTT, slight FP					
EPON 828	10						
Run 5							
48262-38-16 2.98 VOC							
MIBK-DETA	3.5	5 Hours, NFP	F	H	100	100	-24 days ^C
MIBK	10						
EPON 828	10						

Table 5 (cont'd)

FORMULATION		Dry to touch	Hardness (24 hours)		MEK	Double Rubs	Gel time		
Ingredients	Grams		Day 1	Day 5	Day 6	Day 1	Day 5	Day 6	Comments
48262-39-07 2.98 VOC									
MIBK-DETA	3.5	4 hours	H	2H	2H	100	100	12-14 days ^D	Passed direct impact (20 lbs), failed direct impact (40 lbs), passed cross hatch, failed 1/4 inch mandrel bend (2 wks). Amber appearance slight blush, good gloss (<90)
MIBK	5								
EPON 828	10								

^A Reference sample 48220-28-13 used to determine gel time^B Reference sample 48220-53-07 used to determine gel time^C Reference samples 48262-44-09 and 49-07 used to determine gel time^D Reference samples 48220-65-16 used to determine gel time

Another set of tests focused on evaluating reduced VOC formulations. The VOC exempt solvents that were evaluated included acetone and p-chlorobenzotrifluoride (available as Oxsol 100 from Occidental Chemical Corp.). Tertiary butyl acetate (t-butyl acetate), for which exempt status is pending, was also evaluated. The nonexempt solvents included methyl isobutyl ketone (MIBK) and methyl propyl ketone (MPK). The solvents were evaluated in combination with water scavengers, including molecular sieves and Incosol-2® (available from Industrial Copolymers, Ltd.), and several mono and multifunctional reactive diluents. Incosol-2® is a monocyclic bifunctional oxazolidine that reacts with water to form a linear aminoalcohol and an aldehyde.

Eight-five formulations were prepared from xylylenediamine blocked with MIBK. The formulations are shown in Table 6. The materials were dried over mole sieves prior to use. The epoxy resin (EPON 828 available from Miller Stevenson) and the solvent(s) were combined and vortexed for about one minute until the samples were homogenous. Next, the reactive diluent was added, if used. The water scavenger was then added, if used. The samples were vortexed again for about 0.5 to 1.0 minute each, and the blocked amine was added. The samples were vortexed for a third time after which aliquots were transferred to 8 ml glass culture tubes, capped and put in the oven at 55°C for accelerated aging evaluation. The remaining mixtures were maintained at room temperature for approximately 13 to 14 hours.

The results of the testing of these formulations are shown in Tables 7 and 8.

Table 6: Storage Stability Test Matrix Run 20 (MIBK-Xylylenediamine Based System)

Reactive Diluent	742		746		748		757		No Reactive Diluent	
	With Incosol	Without Incosol	With Incosol	Without Incosol	With Incosol	Without Incosol	With Incosol	Without Incosol	With Incosol + 2.5% Excess Amine	With Incosol - 5.0% Excess Amine
MIBK	45C	5C	55C	15C	65C	25C	75C	35C	2C	4C
MPK	47C	7C	57C	17C	67C	27C	77C	37C		
OXSOL 100	49C	9C	59C	19C	69C	29C	79C	39C		
t-Butyl Acetate	51C	11C	61C	21C	71C	31C	81C	41C		
Acetone	53C	13C	63C	23C	73C	33C	83C	43C		

Reactive Diluent	742/TMPTA		746/TMPTA		748/TMPTA		757/TMPTA		No Reactive Diluent	
	With Mole S	Without Mole S	With Mole S	Without Mole S	With Mole S	Without Mole S	With Mole S	Without Mole S	With Mole S + 2.5% Excess Amine	With Mole S - 5.0% Excess Amine
MIBK	46C	6C	56C	16C	66C	26C	76C	36C	1C	3C
MPK	48C	8C	58C	18C	68C	28C	78C	38C		
OXSOL 100	50C	10C	60C	20C	70C	30C	80C	40C		
t-Butyl Acetate	52C	12C	62C	22C	72C	32C	82C	42C		
Acetone	54C	14C	64C	24C	74C	34C	84C	44C		
MIBK/Oxsol 100									85C	

* Ketimine at 2.5 % excess unless otherwise indicated

Table 7: Storage Stability and Physical Property Data Summary of Reduced VOC Formulations Prepared from MIBK-Xylenediamine

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DTT 20	DTT 40	Gloss	Drying Time	Hardness (24H)	Hardness (1 WK)
1C	#N/A	2.68	None	Mole Sieve + 2.5% Excess Amine	MIBK	Fail	72.5	10-12 hours	H	2H	
2C	#N/A	2.68	None	Incisol + 2.5% Excess Amine	MIBK	Pass	Fail	81.2	10 hours	H	2H
3C	19	2.7	None	Mole Sieve - 5.0% Excess Amine	MIBK	Pass	Fail	78	10-12 hours	2H	3H
4C	#N/A	2.67	None	Incisol - 5.0% Excess Amine	MIBK	Pass	Fail	85.5	10-12 hours	H	2H
5C	5.5	2.69	742	None	MIBK	Pass	Pass	47.5	over 10 hours	<B	H
6C	#N/A	2.69	742/TMPTA	None	MIBK	Pass	Fail	103.5	over 10 hours	3H	2H
7C	3.2	2.69	742	None	MPK	Pass	Pass	52.5	over 10 hours	<B	2H
8C	#N/A	2.69	742/TMPTA	None	MPK	Pass	Fail	101	10-12 hours	2H	2H
9C	#N/A	1.33	742	None	OXSOL 100	Pass	Very Slight Fail	61.7	over 10 hours	<B	B
10C	#N/A	1.47	742/TMPTA	None	OXSOL 100	Fail	Fail	100.2	over 10 hours	3H	2H

Table 7 (cont'd)

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	DIT 40	Gloss	Drying Time	Hardness (24H)	Hardness (1 WK)
11C	#N/A	1.48	742	None	t-Butyl Acetate	Pass	Pass	64.2	over 10 hours	<B	H
12C	#N/A	1.61	742/TMPTA	None	t-Butyl Acetate	Pass	Fail	100	over 10 hours	2H	2H
13C	0.85	1.53	742	None	Acetone	Pass	Slight Failure	45.1	over 10 hours	H	2H
14C	#N/A	1.67	742/TMPTA	None	Acetone	Pass	Fail	102.5	10-12 hours	3H	4H
15C	2.8	2.69	746	None	MBK	Pass	Pass	38.3	over 10 hours	<B	2H
16C	#N/A	2.7	746/TMPTA	None	MBK	Fail	Fail	89.5	over 10 hours	2H	2H
17C	2.5	2.69	746	None	MPK	Pass	Pass	34.9	over 10 hours	<B	F
18C	#N/A	2.7	746/TMPTA	None	MPK	Pass	Fail	80.4	over 10 hours	3H	2H
19C	#N/A	1.3	746	None	OXSOL 100	Pass	Pass	48.2	over 10 hours	<B	F
20C	#N/A	1.43	746/TMPTA	None	OXSOL 100	Pass	Fail	97.4	over 10 hours	2H	4H

Table 7 (cont'd)

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	DIT 40	Gloss	Drying Time	Hardness (24H)	Hardness (1 WK)
21C	6.8	1.44	746	None	t-Butyl Acetate	Pass	Pass	45.4	over 10 hours	<B	2H
22C	#N/A	1.58	746/TMPTA	None	t-Butyl Acetate	Pass	Fail	95.4	over 10 hours	2H	3H
23C	2.25	1.49	746	None	Acetone	Pass	Pass	25.5	over 10 hours	<B	F
24C	#N/A	1.63	746/TMPTA	None	Acetone	Pass	Fail	97.1	over 10 hours	2H	2H
25C	1.65	2.7	748	None	MIBK	Pass	Pass	17.6	over 10 hours	<B	F
26C	#N/A	2.69	748/TMPTA	None	MIBK	Pass	Fail	96.7	over 10 hours	H	2H
27C	2	2.7	748	None	MPK	Pass	Pass	31	over 10 hours	<B	HB
28C	#N/A	2.69	748/TMPTA	None	MPK	Pass	Fail	82.7	over 10 hours	2H	2H
29C	13	1.22	748	None	OXSOL 100	Pass	Pass	29.1	over 10 hours	<B	HB
30C	#N/A	1.42	748/TMPTA	None	OXSOL 100	Pass	Fail	90	over 10 hours	2H	2H

Table 7 (cont'd)

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	DIT 40	Gloss	Drying Time	Hardness (24H)	Hardness (1 WK)
31C	5.5	1.37	748	None	t-Butyl Acetate	Pass	Pass	17.3	over 10 hours	<B	<B
32C	#N/A	1.56	748/TMPTA	None	t-Butyl Acetate	Pass	Pass	93	over 10 hours	2H	2H
33C	1.4	1.42	748	None	Acetone	Pass	Pass	33.2	over 10 hours	<B	F
34C	#N/A	1.62	748/TMPTA	None	Acetone	Pass	Pass	98	over 10 hours	2H	4H
35C	#N/A	2.69	757	None	MIBK	Pass	Fail	60.5	10-12 hours	2H	2H
36C	#N/A	2.68	757/TMPTA	None	MIBK	Pass	Fail	99.4	over 10 hours	2H	4H
37C	13	2.69	757	None	MPK	Pass	Slight Failure	52.6	over 10 hours	2H	2H
38C	#N/A	2.68	757/TMPTA	None	MPK	Pass	Fail	99.1	10-12 hours	2H	4H
39C	#N/A	1.38	757	None	OXSOL 100	Pass	Slight Failure	72	10-12 hours	H	2H
40C	#N/A	1.48	757/TMPTA	None	OXSOL 100	Pass	Pass	99.6	over 10 hours	3H	4H
41C	#N/A	1.53	757	None	t-Butyl Acetate	Pass	Very Slight Fail	63.3	over 10 hours	F	2H

Table 7 (cont'd)

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	DIT 40	Gloss	Drying Time	Hardness (24H)	Hardness (1 WK)
42C	#N/A	1.62	757/TMPTA	None	t-Butyl Acetate	Pass	Fail	99.4	over 10 hours	2H	2H
43C	4.4	1.58	757	None	Acetone	Pass	Slight Failure	60.8	10-12 hours	H	H
44C	#N/A	1.68	757/TMPTA	None	Acetone	Pass	Fail	101.9	over 10 hours	4H	4H
45C	5.5	2.69	742	Incisol	MBK	Pass	Pass	35	10-24 hours	<B	B
46C	#N/A	2.69	742/TMPTA	Mole Sieve	MBK	Pass	Fail	101.3	10-24 hours	2H	4H
47C	3.2	2.69	742	Incisol	MPK	Pass	Pass	29.6	10-24 hours	<B	<B
48C	#N/A	2.69	742/TMPTA	Mole Sieve	MPK	Pass	Fail	98.5	10-24 hours	H	2H
49C	#N/A	1.32	742	Incisol	OXSOL 100	Pass	Pass	54.5	10-24 hours	<B	HB
50C	#N/A	1.47	742/TMPTA	Mole Sieve	OXSOL 100	Pass	Fail	95.4	10-24 hours	2H	2H
51C	13	1.46	742	Incisol	t-Butyl Acetate	Pass	Pass	54.5	10-24 hours	HB	HB
52C	#N/A	1.61	742/TMPTA	Mole Sieve	t-Butyl Acetate	Pass	Fail	88.4	10-24 hours	2H	2H
53C	0.85	1.52	742	Incisol	Acetone	Pass	Very Slight Fail	42.5	10-24 hours	<B	F
54C	2.8	1.67	742/TMPTA	Mole Sieve	Acetone	Pass	Fail	101.2	10-24 hours	2H	4H

Table 7 (cont'd)

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	DIT 40	Gloss	Drying Time	Hardness (24H)	Hardness (1 WK)
55C	2.5	2.69	746	Incisol	MBK	Pass	Pass	32.3	10-24 hours	<B	HB
56C	#N/A	2.7	746/TMPTA	Mole Sieve	MBK	Pass	Slight Failure	84	10-24 hours	2H	2H
57C	1.65	2.69	746	Incisol	MPK	Pass	Pass	21	10-24 hours	<B	B
58C	13	2.7	746/TMPTA	Mole Sieve	MPK	Pass	Pass	94.5	10-24 hours	2H	4H
59C	#N/A	1.29	746	Incisol	OXSOL 100	Pass	Pass	45.6	10-24 hours	<B	H
60C	#N/A	1.43	746/TMPTA	Mole Sieve	OXSOL 100	Pass	Fail	92.3	10-24 hours	H	4H
61C	5.5	1.43	746	Incisol	t-Butyl Acetate	Pass	Fail	38.5	10-24 hours	F	H
62C	#N/A	1.58	746/TMPTA	Mole Sieve	t-Butyl Acetate	Pass	Fail	93.2	10-24 hours	3H	3H
63C	1.25	1.48	746	Incisol	Acetone	Pass	Pass	24.4	10-24 hours	F	F
64C	3.7	1.63	746/TMPTA	Mole Sieve	Acetone	Pass	Slight Failure	99.2	10-24 hours	2H	4H
65C	2.25	2.7	748	Incisol	MBK	Pass	Pass	16.9	10-24 hours	H	B
66C	#N/A	2.69	748/TMPTA	Mole Sieve	MBK	Pass	Pass	94	10-24 hours	H	4H
67C	1.4	2.7	748	Incisol	MPK	Pass	Pass	15.3	10-24 hours	<B	B

Table 7 (cont'd)

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	DIT 40	Gloss	Drying Time	Hardness (24H)	Hardness (1 WK)
68C	13	2.69	748/TMPTA	Mole Sieve	MPK	Pass	Pass	96.2	10-24 hours	H	2H
69C	#N/A	1.21	748	Incisol	OXSOL 100	Pass	Pass	21.6	10-24 hours	<B	B
70C	#N/A	1.42	748/TMPTA	Mole Sieve	OXSOL 100	Pass	Fail	91.2	10-24 hours	2H	3H
71C	4.7	1.36	748	Incisol	t-Butyl Acetate	Pass	Pass	22.8	10-24 hours	<B	F
72C	#N/A	1.46	748/TMPTA	Mole Sieve	t-Butyl Acetate	Pass	Pass	83.6	10-24 hours	H	2H
73C	0.65	1.41	748	Incisol	Acetone	Pass	Pass	36.9	10-24 hours	<B	<B
74C	3.7	1.62	748/TMPTA	Mole Sieve	Acetone	Pass	Pass	91	10-24 hours	H	4H
75C	#N/A	2.69	757	Incisol	MIBK	Pass	Slight Failure	50.7	10-24 hours	2H	2H
76C	#N/A	2.68	757/TMPTA	Mole Sieve	MIBK	Pass	Fail	92.1	10-24 hours	2H	4H
77C	9	2.69	757	Incisol	MPK	Pass	Slight Failure	45.5	10-24 hours	F	F
78C	#N/A	2.68	757/TMPTA	Mole Sieve	MPK	Pass	Pass	96.8	10-24 hours	2H	4H
79C	#N/A	1.37	757	Incisol	OXSOL 100	Pass	Pass	65	10-24 hours	H	2H
80C	#N/A	1.48	757/TMPTA	Mole Sieve	OXSOL 100	Pass	Pass	94.9	10-24 hours	2H	4H

Table 7 (cont'd)

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	DIT 40	Gloss	Drying Time	Hardness (24H)	Hardness (1 WK)
81C	#N/A	1.51	757	Incisol	t-Butyl Acetate	Pass	Pass	62.7	10-24 hours	<B	2H
82C	#N/A	1.62	757/TMPTA	Mole Sieve	t-Butyl Acetate	Pass	Pass	93.7	10-24 hours	2H	>4H
83C	2.5	1.68	757	Incisol	Acetone	Pass	Slight Failure	49.6	10-24 hours	F	F
84C	5.5	1.63	757/TMPTA	Mole Sieve	Acetone	Pass	Pass	95.1	10-24 hours	H	4H
85C	0.5	3.05	None	Mole Sieve	MBK/ OXSOL 100	Pass	Very Slight Fail	76.5	10-24 hours	H	2H

Table 8: Overall Film Evaluations Based on Visual Observations

Sample ID	Comments
1C	Irregular flow pattern & lower gloss indicate some incompatibility
2C	Irregular flow pattern & high low gloss indicate some incompatibility
3C	Fairly good flow and gloss but brittle film
4C	Good gloss and flow but brittle film
5C	Good flow but "high-low" gloss pattern indicates incompatibility
6C	Excellent gloss, good flow but brittle film
7C	Good flow but "high-low" gloss pattern indicates incompatibility
8C	Excellent flow & gloss but brittle film
9C	Good flow but "high-low" glass pattern indicates incompatibility
10C	Excellent gloss, good flow but very brittle film
11C	Good flow but "high-low" gloss pattern indicates incompatibility
12C	Excellent gloss & flow but brittle film
13C	Classic example of "high low" gloss pattern & incompatibility
14C	Excellent gloss & flow but brittle film
15C	Good flow but poor gloss
16C	Good gloss, excellent flow but brittle film
17C	Good flow, poor gloss, good flexibility
18C	Good flow & gloss but slight haze; brittle film
19C	Excellent flow but poor gloss; flexible film
20C	Excellent gloss & flow but brittle film
21C	Excellent flow but poor gloss; flexible film
22C	Excellent flow & good but brittle film
23C	Good flow, poor gloss but brittle film
24C	Outstanding gloss & flow but brittle film
25C	Poor gloss & flow; blush
26C	Excellent gloss, moderate flow; brittle film
27C	Low gloss, moderately good flow; blush; flexible film
28C	Fairly good flow but irregular gloss indicates incompatibility
29C	Poor gloss; blush, but good flexible film
30C	Excellent gloss; irregular flow; brittle film
31C	Very poor gloss; film soft, mars easily
32C	Excellent gloss; erratic flow pattern; flexible film
33C	Poor flow pattern, low gloss due to incompatibility
34C	Outstanding gloss, flow hardness & flexibility (*)
35C	Classic "high-low" gloss pattern of incompatibility

Table 8 (cont'd)

36C	Outstanding gloss, erratic flow pattern; brittle film
37C	“high-low” gloss, erratic flow reflects incompatibility
38C	Good gloss & flow but brittle film
39C	“High-low” gloss, erratic flow reflects incompatibility
40C	Excellent gloss, slightly erratic flow, but good flexibility
41C	High-low gloss, erratic flow; incompatibility, flexible film
42C	Outstanding gloss & flow; brittle film
43C	“High-low” gloss; erratic flow reflect incompatibility
44C	Outstanding gloss, good-flow but brittle film
45C	Poor gloss, “high-low” gloss; incompatible but flexible
46C	Outstanding gloss, good flow but brittle film
47C	Poor gloss (“high-low”) reflect incompatibility flexible film
48C	Outstanding gloss, very good flow but brittle film
49C	Good flow pattern & flexibility but poor gloss
50C	Very good gloss & flow but brittle film
51C	Good flow & flexibility but poor gloss
52C	Good gloss; fairly good flow but brittle film
53C	Classic “high-low” gloss pattern; incompatible flexible film
54C	Outstanding gloss; very good flow but brittle film
55C	Poor flow and gloss; incompatible but flexible film
56C	Very good gloss, flow and relatively good flexibility
57C	Poor flow & gloss; incompatible but flexible film
58C	Outstanding gloss, flow, hardness & flexibility *
59C	Poor flow & gloss; blush, but flexible film
60C	Good gloss & flow but brittle film
61C	Good flow but poor gloss flexible film
62C	Good gloss & glow but brittle film
63C	Poor gloss & flow; incompatible but flexible films
64C	Excellent gloss & flow but brittle film
65C	Poor gloss and flow; soft film; mars easily; blush
66C	Very good gloss, flow & flexibility
67C	Poor gloss; good flow & flexible film
68C	Very good gloss, flow, hardness & flexibility *
69C	Poor gloss; film soft; mars easily, flexible film
70C	Good gloss & flow but brittle film
71C	Poor gloss; film soft, mars easily but flexible
72C	Gloss & flexibility good but “mottled” flow is a problem
73C	Poor gloss, poor flow film soft & mars easily

Table 8 (cont'd)

74C	Very good gloss, flow, hardness & flexibility *
75C	"High-low" gloss pattern reflects incompatibility
76C	Excellent gloss slightly erratic flow & brittle film
77C	Classic "high-low" gloss incompatibility
78C	Very good gloss, flow, hardness & flexibility *
79C	Nice looking film but poor gloss; film flexible
80C	Very good gloss, flow, hardness & flexibility *
81C	Nice looking film but poor gloss, film flexible
82C	Good gloss & flow, hardness & flexibility
83C	"High-low" gloss pattern reflects incompatibility
84C	Very good gloss, flow, hardness & flexibility *
85C	Nice looking film but haze hinders gloss flexible.

Note: Incompatibility in the strictest sense refers to the fact that a portion of the film appears to be insoluble in the residual solvent or reactive diluents.

* Superior film in all aspects except (slightly reduced) gloss.

After 30 days of accelerated aging, thirty-five of the eighty-five formulation evaluated had measured viscosities of 16 stokes or less, as shown in Table 9. The VOC level of these formulations ranged from 1.22 to 3.05 lbs/gal.

Of those 35 formulations, 29 had viscosities of 7 stokes or less, as shown in Table 10. The VOC level for these formulations ranged from 1.36 to 3.05 lbs/gal.

Of the 29 formulations with viscosities of 7 stokes or less, 12 contained Incosol-2® as a water scavenger, 12 contained no water scavenger, and five contained mole sieves. Only the mole sieves were tested in combination with the reactive diluent trimethylolpropanetriacrylate (TMPTA). The formulations containing TMPTA gelled faster than formulations without TMPTA, regardless of the solvent. In addition, six of the 20 TMPTA/mole sieve formulations remained sprayable after thirty days of accelerated aging. None of the samples containing TMPTA without mole sieves maintained acceptable viscosities after thirty days of accelerated aging.

Five formulations had a viscosity of 1.25 stokes or less and remained water-like. The VOC level for these formulations ranged from 1.41 to 3.05 lbs/gal. Samples 13C, 53C, 63C, and 73C contained acetone as a solvent and sample 85C contained equal parts of acetone and p-chlorobenzotrifluoride as a solvent. None of the five samples contained a multifunctional reactive diluent. Thin films made from these formulations were characterized by low gloss and inadequate hardness.

Draw-down panels were prepared with a #54 wire bound rod over Bonderite 1000 iron phosphate treated steel panels that were 3" x 6" x 0.0032". The panels were held at a constant temperature of 75°F/50 RH and then observed at two-hour increments for ten hours to determine drying time. The majority of the panels required 10-12 hours or more before they were dry to the touch. The samples evaluated in the first phase using the same ketimine dried in 8 -10 hours. The slower drying time is attributable to three factors. First, formulations in the second phase had a 2.5 wt % excess amine instead of 5 wt % as used in the first phase experiments. Second, the average coating thickness was 1.83 mils, due to the higher percent solids associated with the panel, rather than about 0.8 mils as in the previous panels. Finally, the constant temperature

room was 73°F/45% RH during the thin film dry period, whereas, the previous panels were maintained in a constant temperature room at 75°F/50% RH. These conditions are slightly less favorable and would slightly retard cure time.

Comparing the effects of the reactive diluents on the coatings, the panels containing TMPTA as a reactive diluent had better hardness and gloss. Among the Epoxy reactive modifiers, Epoxy 757, a bifunctional epoxy resin, also exhibited good gloss and hardness. Since the other reactive diluents are monofunctional, these results are consistent with conventional coating chemistry. In summary, independent of VOC levels and storage stability, many test panels show excellent hardness and gloss while still maintaining sufficient flexibility to pass the impact testing.

Four formulations remained sprayable after 30 days of accelerated aging at 55°C regardless of base solvent, had gloss values of greater than or equal to 85, passed both 20/40 pound impact testing, and had a pencil hardness of greater than or equal to H after 1 week. The four formulations that met the above criteria are 58C, 68C, 74C, and 84C. Two of these contain MPK as a solvent (Samples 58C and 68C), and two contain acetone (Samples 74C and 84C). The viscosity of both MPK formulations was 13 stokes at day 30, which puts the viscosities around the middle of the acceptable range. As a result, these formulations should remain easily sprayable for months, have acceptable VOC levels (2.7 and 2.69 lbs/gal, respectively), and good physical properties. Samples 74C and 84C have very low VOC levels (1.62 and 1.63 lbs/gal, respectively) and retained near water-like viscosities after accelerated aging for 30 days.

Many of the samples maintained acceptable viscosities for about six months or more, based on accelerated aging projection, with acceptable physicals and VOC levels.

Table 9: Formulations With Viscosities \leq 16 Stokes After 30 Days of Accelerated Aging At 55°C

Sample ID	Viscosity at 30 Days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	Gloss	Hardness (1WK)
5C	5.5	2.69	742	None	MIBK	Pass	47.5	H
7C	3.2	2.69	742	None	MPK	Pass	52.5	2H
13C	0.85	1.53	742	None	Acetone	Pass	45.1	2H
15C	2.8	2.69	746	None	MIBK	Pass	38.3	2H
17C	2.5	2.69	746	None	MPK	Pass	34.9	F
21C	6.8	1.44	746	None	t-Butyl Acetate	Pass	45.4	2H
23C	2.25	1.49	746	None	Acetone	Pass	25.5	F
25C	1.65	2.7	748	None	MIBK	Pass	17.6	F
27C	2	2.7	748	None	MPK	Pass	31	HB
29C	13	1.22	748	None	OXSOL 100	Pass	29.1	HB
31C	5.5	1.37	748	None	t-Butyl Acetate	Pass	17.3	<B
33C	1.4	1.42	748	None	Acetone	Pass	33.2	F
37C	13	2.69	757	None	MPK	Pass	52.6	2H
43C	4.4	1.58	757	None	Acetone	Pass	60.8	H
45C	5.5	2.69	742	Incosol	MIBK	Pass	35	B
47C	3.2	2.69	742	Incosol	MPK	Pass	29.6	<B
51C	13	1.46	742	Incosol	t-Butyl Acetate	Pass	54.5	HB
53C	0.85	1.52	742	Incosol	Acetone	Pass	42.5	F
54C	2.8	1.67	742/TMPTA	Mole Sieve	Acetone	Pass	101.2	4H
55C	2.5	2.69	746	Incosol	MIBK	Pass	32.3	HB
57C	1.65	2.69	746	Incosol	MPK	Pass	21	B
58C	13	2.7	746/TMPTA	Mole Sieve	MPK	Pass	94.5	4H
61C	5.5	1.43	746	Incosol	t-Butyl Acetate	Pass	38.5	H
63C	1.25	1.48	746	Incosol	Acetone	Pass	24.4	F
64C	3.7	1.63	746/TMPTA	Mole Sieve	Acetone	Pass	99.2	4H
65C	2.25	2.7	748	Incosol	MIBK	Pass	16.9	B
67C	1.4	2.7	748	Incosol	MPK	Pass	15.3	B
68C	13	2.69	748/TMPTA	Mole Sieve	MPK	Pass	96.2	2H
71C	4.7	1.36	748	Incosol	t-Butyl Acetate	Pass	22.8	F
73C	0.65	1.41	748	Incosol	Acetone	Pass	36.9	<B
74C	3.7	1.62	748/TMPTA	Mole Sieve	Acetone	Pass	91	4H

Table 9 (cont'd)

77C	9	2.69	757	Incosol	MPK	Pass	45.5	F
83C	2.5	1.68	757	Incosol	Acetone	Pass	49.6	F
84C	5.5	1.63	757/TMPTA	Mole Sieve	Acetone	Pass	95.1	4H
85C	0.5	3.05	None	Mole Sieve	MIBK/ Oxsol 100	Pass	76.5	2H

Table 10: Formulations With Viscosities ≤ 7 Stokes After 30 Days of Accelerated Aging At 55°C

Sample ID	Viscosity @30 days	VOC	Reactive Diluent	Scavenger	Solvent System	DIT 20	DIT 40	Gloss (24H)	Hardness (1WK)
5C	5.5	2.69	742	None	MIBK	Pass	Pass	47.5	<B
7C	3.2	2.69	742	None	MPK	Pass	Pass	52.5	<B
13C	0.85	1.53	742	None	Acetone	Pass	Slight Failure	45.1	H
15C	2.8	2.69	746	None	MIBK	Pass	Pass	38.3	<B
17C	2.5	2.69	746	None	MPK	Pass	Pass	34.9	<B
21C	6.8	1.44	746	None	t-Butyl Acetate	Pass	Pass	45.4	<B
23C	2.25	1.49	746	None	Acetone	Pass	Pass	25.5	<B
25C	1.65	2.7	748	None	MIBK	Pass	Pass	17.6	<B
27C	2	2.7	748	None	MPK	Pass	Pass	31	<B
31C	5.5	1.37	748	None	t-Butyl Acetate	Pass	Pass	17.3	<B
33C	1.4	1.42	748	None	Acetone	Pass	Pass	33.2	<B
43C	4.4	1.58	757	None	Acetone	Pass	Slight Failure	60.8	H
45C	5.5	2.69	742	Incosol	MIBK	Pass	Pass	35	<B
47C	3.2	2.69	742	Incosol	MPK	Pass	Pass	29.6	<B
53C	0.85	1.52	742	Incosol	Acetone	Pass	Very Slight Fail	42.5	<B
54C	2.8	1.67	742/TMPTA	Mole Sieve	Acetone	Pass	Fail	101.2	2H
55C	2.5	2.69	746	Incosol	MIBK	Pass	Pass	32.3	<B
57C	1.65	2.69	746	Incosol	MPK	Pass	Pass	21	<B
61C	5.5	1.43	746	Incosol	t-Butyl Acetate	Pass	Fail	38.5	F
63C	1.25	1.48	746	Incosol	Acetone	Pass	Pass	24.4	F
64C	3.7	1.63	746/TMPTA	Mole Sieve	Acetone	Pass	Slight Failure	99.2	2H
65C	2.25	2.7	748	Incosol	MIBK	Pass	Pass	16.9	H
67C	1.4	2.7	748	Incosol	MPK	Pass	Pass	15.3	<B
71C	4.7	1.36	748	Incosol	t-Butyl Acetate	Pass	Pass	22.8	<B

Table 10 (cont'd)

	73C	0.65	1.41	748	Incisol	Acetone	Pass	Pass	36.9	<B	<B
	74C	3.7	1.62	748/TMPTA	Mole Sieve	Acetone	Pass	Pass	91	H	4H
83C	2.5	1.68	757	Incisol	Acetone	Pass	Slight Failure	49.6	F	F	
84C	5.5	1.63	757/TMPTA	Mole Sieve	Acetone	Pass	Pass	95.1	H	4H	
85C	0.5	3.05	None	Mole Sieve	MBK/Oxsol	Pass	Very Slight Fail	76.5	H	2H	
					100						

The effect of different solvents was also evaluated. Table 11 shows the effect of various solvents using two different blocked amines: DETA blocked with MIBK, and xylylenediamine blocked with MIBK. The solvents from best to worst, regardless of reactive modifier or water scavenger, with respect to hindering gelation were: acetone, MPK, MIBK, t-butyl acetate, and p-chlorobenzotrifluoride. The inability of t-butyl acetate to hinder gelation could be due to the presence of 0.5-1.0% t-butyl alcohol, an impurity that could react with the epoxy resin.

A mixed solvent system comprised of equal parts p-chlorobenzotrifluoride/MIBK was evaluated (Sample 85C). The formulation showed no increase in viscosity after 30 day of accelerated aging. The calculated VOC level of the formulation was 3.05 lbs/gal, which is slightly higher than the target value of 2.8 lbs/gal. Other physical property values were good. Sample 85C displayed no viscosity increase although p-chlorobenzotrifluoride alone is the least effective solvent at retarding gelation.

Although not wishing to be bound by theory, we believe that these results are a function of the polarity and hydrogen bonding of the solvents. Table 12 shows a ranking of solvents and their polarity solubility parameters and hydrogen bonding solubility parameters. Oxygen containing solvent systems having both intermediate to high polarity (α_P of 6-14) and high hydrogen bonding (α_H of 9-14) are unacceptable for stable coating formulations. Systems with both low polarity (α_P of 1-2) and low to intermediate hydrogen bonding capabilities (α_H of 2-7) have poor capacity to stabilize a blocked amine epoxy coating precursor. Oxygenated solvents with intermediate polarity (α_P of 5-10) and intermediate hydrogen bonding (α_H of 4-7) are acceptable for stable single component epoxy coating precursors.

Thus, single component epoxy coating precursors made from blocked amines having an extended shelf life have been demonstrated. Coatings can made from these precursors having VOC levels of less than 3 lbs/gal.

Coating formulations made according to the present invention may contain additional components, including, but not limited to, pigments, such as titanium dioxide, fillers, such as silica, and other formulation aids, such as wetting agents, defoamers, flow aids, leveling agents, and the like.

Table 11: Effect of Solvent System on High Temperature Storage Stability and Solution Viscosity

Ketimine + Epoxy Resin	Solvent	Stability at 55°C (Viscosity) (Stokes)
DETA-MIBK	Toluene	None
	MIBK	Sprayable after 15 days
	50/50 Toluene/MIBK	None
Xylylenediamine-MIBK	MIBK (a)	19 after 30 days
	MIBK (b)	5.5 after 30 days
	MPK (c)	3.2 after 30 days
	p-chlorobenzotrifluoride (d)	gelled after 30 days
	50/50 MIBK/p-chlorobenzotrifluoride (e)	0.5 after 30 days
	t-butyl acetate (f)	13 after 30 days
	acetone (g)	0.85 after 30 days

(a) contains mole sieves but no reactive diluent

(b) contains monofunctional reactive diluent (Epodil™ 742) but no scavenger

(c) contains monofunctional reactive diluent (Epodil™ 742) but no scavenger

(d) contains monofunctional reactive diluent (Epodil™ 742) but no scavenger

(e) contains moles sieves but no reactive diluent

(f) contains Incosol-2™ and monofunctional reactive diluent (Epodil™ 742)

(g) contains Incosol-2™ and monofunctional reactive diluent (Epodil™ 742)

Table 12: Ranking of Solvents for Stability of Xylylenediamine-MIBK Epoxy Coatings

Solvents	Ranking	Polarity (δP)	Hydrogen Bonding (δH)
Acetone	Good	10.4	7
MIBK	"	6.1	4.1
MPK	"	--	--
Ethyl Acetate	"	5.3	7.2
Dioxane	Poor	1.8	7.4
T-butyl acetate	"	--	--
Toluene	"	1.4	2
P-chlorobenzo trifluoride	Unacceptable	--	--
Dimethylformamide	"	13.7	11.3
Benzyl Alcohol	"	6.3	13.7

δP - Polar solubility parameter (MPa^{1/2})

δH - Hydrogen bonding solubility parameter (MPa^{1/2})

While certain representative embodiments and details have been shown for purposes of illustrating the invention, it will be apparent to those skilled in the art that various changes in the compositions and methods disclosed herein may be made without departing from the scope of the invention, which is defined in the appended claims.